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A comprehensive study on methane storage capacity of anthracites based activated carbons; a compromise between BET surface area and bulk density

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Abstract

The present study investigates the effect of preparation variables of AC on the optimum amount of BET surface area and bulk density for methane adsorption purposes. All activated carbons samples were synthesized through the chemical activation method, using KOH chemical agent. The effect of preparation parameters including chemical impregnation ratio and activation temperatures was evaluated on two important characteristics of microporosity and bulk density. The best performance of the AC sample was observed at a KOH/anthracite chemical ratio of 3, activation temperature of 730^{o}C. At the optimum condition, the activated carbon acquired convenient microporosity in the matrix structure, with BET surface area of 2160 m^2/g packing density of 0.53 g/cm^3 and methane adsorption capacity of 175 V/V.

Keywords: *Microporosity, Bulk density, Methane storage, Activated carbon.*

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1. Introduction

Natural gas is the preferable type of fuel in comparison with other conventional sources of energy. The highest advantage of natural gas, which is mainly composed of methane, is that it is cheaper than gasoline and widely available in many countries [1]. Adsorbed natural gas as an alternative energy source using a porous material, could reduce the methane storage pressure to around 1/5-1/6 of CNG at ambient temperature.

Among all conventional adsorbent for methane storage including zeolites [2], metal-organic frameworks [3, 4], and activated carbons (ACs) [5], microporous carbon is one the most promising adsorbents in ANG technology. Conventional precursors such as coals, nutshells, polymers and various chemical reagents like phosphoric acid, zinc chloride, sodium carbonate, sodium hydroxide and potassium hydroxide have been employed for the synthesis of activated carbons [1, 6-9]. To obtain high methane adsorption capacity in ANG storage tanks, many studies have recommended chemical activation process by using anthracite as a precursor and KOH as a chemical agent [10-13].

The Department of Energy of the United States (DOE) established a volumetric objective for the adsorbed natural gas value of 150 cm^3 (STP: 0ºC, 1 bar)/cm^3 in 1995, which was elevated to 263 cm^3 (STP: 0ºC, 1 bar)/cm^3, recently. To achieve this target the adsorbent must have appropriate BET surface area along with a narrow pore size distribution, between 0.8 and 1.1 nm. For the ANG purposes, it is necessary to consider packing density along with microporosity of the adsorbent, simultaneously.

This research deals with the preparation parameters of activated carbon from local anthracite (from Iranian mine) as the precursor, with the objective of packing density and microporosity to attain maximum methane adsorption. To achieve this goal, about 7 different experiments were designed to investigate the effect of input parameters of impregnation ratio and activation temperature on the BET, packing density and methane adsorption.

In this paper, two different views are underlined: a) providing experimental data for preparation of AC with anthracite as a precursor and KOH as a chemical agent under various operational conditions, which is essential for accurate analysis of the entire process, and b) considering the impact of both packing density along with microporosity on methane uptake of anthracite-based on ACs. To the best our knowledge, this approach has not been adopted in previous researches and the results of this paper can make a significant improvement in methane storage capacity in ANG application.

2. Materials and Methods

2.1 Materials

Anthracite precursor was obtained from Mazinoo mine in the southern Khorasan province (Iran coal mining pole) and elemental analysis was conducted using the ASTM method [14]. High purity chemical substances such as potassium hydroxides, hydrochloric acid, sodium thiosulfate, iodine, potassium iodide, potassium iodate, starch and sodium carbonate were purchased from Merck KGA (Germany). Methane

with ultra-high purity 99.999% and nitrogen with stated purity of 99% were supplied by UAE and Iran, respectively.

2.2 Preparation and activation procedure

Anthracite was grounded and sieved to grain particles with an average size of 250–500 µm. Afterward, the powder was retained in the oven and dried at 120ºC for one day to ensure that the moisture content of products was eliminated. Before each activation run, curtained amount of anthracite powder was physically mixed with the potassium hydroxide powder. Then, the mixture was loaded into a special stainless-steel boat and heated up at a rate of 5 K/min in a horizontal tubular furnace under a nitrogen flow of 650 mL/min. After a specified residence time, the furnace was cooled down at room temperature under constant nitrogen flow. The product was washed with HCl 1M and then rinsed with distilled water to reach neutral pH (about 6.5). The final ACs samples were obtained by drying the washed ACs in the oven at 130ºC for 24 h. The synthesis conditions for each sample were listed in Table 1.

Table 1. Pyrolysis conditions of the petroleum residues.

Number	Impregnation ratio	Activation temperatures (°C)	Residence time (min)	Nomenclature
1	3	700	60	AC3700
2	3	750	60	AC3750
3	3	800	60	AC3800
4	3.5	700	60	AC35700
5	3.5	750	60	AC357500
6	4	700	60	AC4700
7	4	800	60	AC4800

2.3 Characterization of activated carbon

According to the standard test method of ASTM D7582–10, the elemental analysis of anthracite was determined.

Nitrogen adsorption data were used to determine: i) the BET specific surface area (S_{BET}), ii) the total pore volume (Vt) at a relative pressure of 0.95 and iii) the micropore volume (Vmi) at pores < 2 by applying the total pore volume (NLDFT).

Packing density has been determined by pressing a given mass of activated carbon in a mold with a cross-sectional area of 1.30 m^2 at a pressure of 500 kg/cm^2 [6]. The measurements were repeated several times and the final densities had an error rate of less than 3%.

The methane adsorption capacity of the AC samples was estimated at 25ºC and up to a pressure of 4 MPa. Prior to the adsorption measurement, activated carbons were degassed at 200ºC for 5 h via heating and vacuuming. Figure 1 shows the experiment was carried out in homemade manometric equipment. Helium is used to calculate the void space.

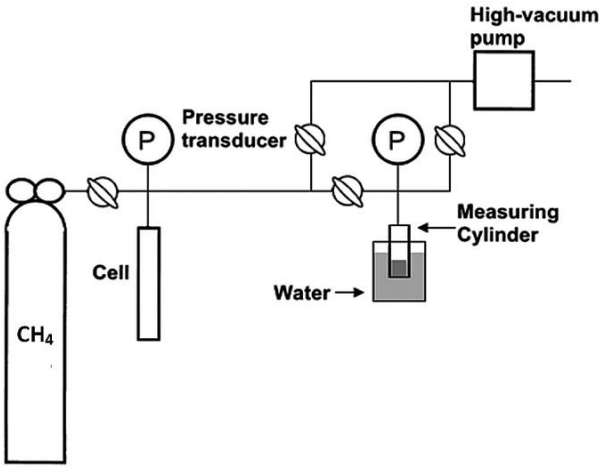

Figure 1. Schematic diagram of the volumetric device for methane adsorption

3. Results and Discussion

The experimental results obtained along the study will be discussed in the following sections as terms of the effect the activation conditions (the ratio of Precursor: KOH and temperature) on both characteristics of microporosity development and packing density of synthesized activated carbon for the methane storage applications.

3.1 Effect of the impregnation ratio

Accurate results from the elemental analysis of AC samples provides valuable information about the chemical composition of raw material. The information data including fixed carbon, ash, volatile matter and moisture contents are summarized in Table 2.

Table 2. Elemental analysis of anthracite

Proximate Analysis			
Carbon (%)	**Ash (%)**	**Volatile matter (%)**	**Moisture (%)**
86	8.1	5.4	0.5

The nitrogen adsorption-desorption isotherms for the samples of AC3700, AC35700 and AC4700 are presented in Figure 2. The isotherms clearly show the effect of precursor: KOH ratio on the activation process.

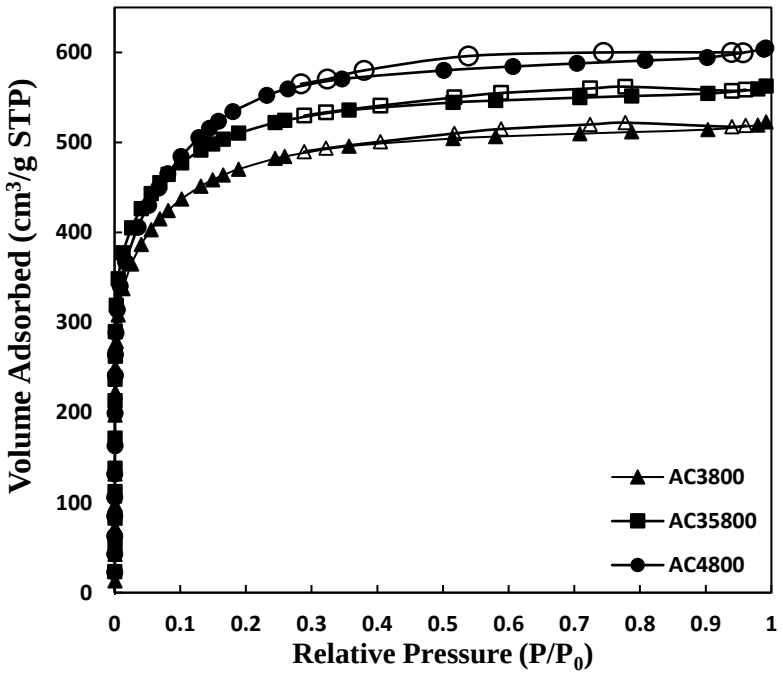

Figure 2. N_2 adsorption isotherms for samples of AC3800, AC35800 and AC4800. Filled and empty signs are representative for N_2 adsorption and desorption data, respectively.

The graph shows that there has been a steady rise trend between impregnation ratio and the amount of N_2 uptake. This finding stresses the fact that the higher porosity development is reached by more value of a chemical agent.

Activated sample with a ratio of 1 (precursor): 3 (KOH) shows a narrow knee indicating the presence of a narrow pore size distribution (PSD). There is a second group of isotherms for samples activated using ratios above 4:1 which exhibit a wider knee in the nitrogen adsorption isotherm, thus suggesting the development of wider micropores. These experimental findings suggested that the larger amount of impregnation ratio exhibit a wider knee in the nitrogen adsorption isotherm, resulting exhibit a wider knee in the nitrogen adsorption isotherm.

3.2 Effect of the activation temperature

Nitrogen adsorption isotherm was determined at three different temperature of 700, 750 and 800ºC for ACs samples using a fixed ratio of 1:3. The finding results are presented in Figure 3. These isotherms clearly show that the higher the activation temperature, the wider the knee of the isotherm. On the other hand, a decrease in the activation temperature brings a narrowing of the pore size distribution. The similar observation was also reported by Liu et al for coal-derived activated carbon [15], Daud et al. for palm-shell-derived activated carbon [16] and Gergova et al. for pit-derived activated carbon [17].

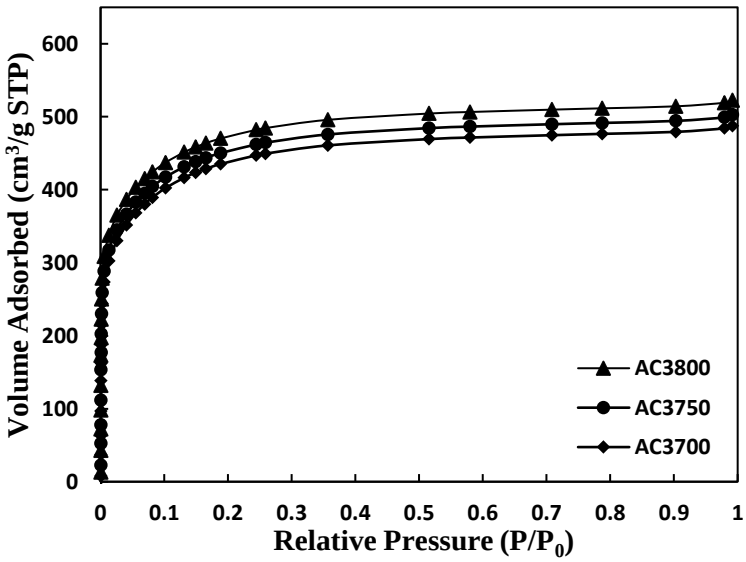

Figure 3. N_2 adsorption isotherms for samples of AC4700, AC4750 and AC4800. Filled and empty signs are representative for N_2 adsorption and desorption data, respectively.

To sum up, first, the anthracite-based adsorbent was synthesized at different preparation condition of chemical impregnation ratio and temperatures. All prepared ACs were tested by nitrogen adsorption/desorption isotherm to eliminate most of the mesoporosity. Also, packing density for all ACs samples, as a pivotal factor for methane storage in volumetric was measured. In the following section, the performance of these materials on methane adsorption will be discussed.

Table 3. Textural characteristic and methane uptake at 25ºC and 4 Mpa.

Sample	S_{BET} (m^2/g)	Density (g/cm)	Methane uptake (V/V)
AC3700	2280	0.54	167
AC3750	2305	0.52	163
AC3800	2420	0.45	145
AC35700	2495	0.44	160
AC357500	2517	0.40	160
AC4700	2041	0.62	155
AC4800	2533	0.38	159

3.3 Methane adsorption

Both characteristics of S_{BET} and packing density are very important to evaluate the behavior of the adsorbent in case of maximum methane storage. In addition, the adsorbent must exhibit a narrow pore size distribution, centered at around 0.8-1.2 nm, which is an effective pore size to accommodate two or three molecules of methane. Under these circumstances, the packing density of the ACs adsorbents achieves a maximum value. A clear relationship between the amount of methane adsorbed at 4

MPa and both important characteristics of S_{BET} and packing density was found in Figure 4.

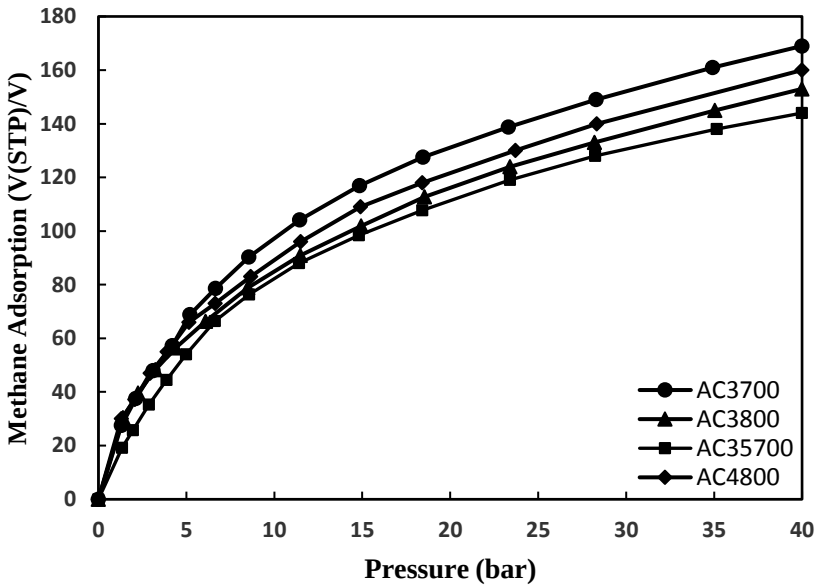

Figure 4. Methane adsorption isotherm at 25ºC up to 40 bar for the samples of AC3700, AC3800, AC35700 and AC4800 in volumetric basis

The experimental findings of the methane isotherms were in good agreement with previous results described in the cited literature [6, 18, 19]. Packing density as an important factor should be considered along with microporosity of the ACs sample for ANG application. It is obvious by the figure that the sample of AC4800 with the highest BET surface area shows low methane storage capacity in comparison with AC3700. Interestingly, the highest value of methane adsorption was obtained for sample AC3700, where a compromise between packing density and micropore volume was reached. It is clear from Table 3, that AC3700 possesses the medium level of microporosity and packing density among all adsorbents. While AC4800 owns the maximum microporosity and minimum amount of packing density. In general speaking, the activated carbon prepared at low temperature and impregnation ratio has a more compact structure in comparison with the others. These results stress the importance of porous texture property along with the packing density of adsorbents in ANG application.

Interestingly, the sample of AC3700 presents methane uptakes near 167 that is very close to the 2002 DOE target by only increasing pressure from 4 to 5 MPa. The superior performance of the mentioned sample can make a significant improvement in methane storage capacity for ANG applications.

4. Conclusion

Preparation conditions of anthracite-based adsorbents have been optimized in terms of developing a very high methane adsorption capacity together with a high packing density. The samples were characterized by elemental analysis, nitrogen adsorption isotherm, packing density and methane storage capacity. The maximum amount of microporosity was reached at impregnation ratio of 1 (precursor)/ 4 (KOH). The precursor/KOH ratio of 1:3 is optimum to obtain a most favorable porosity development with a narrow pore size distribution. The activation temperature of activation of 700ºC guarantees the improvement in methane adsorption properties of the related sample. Interestingly, at the above-mentioned activated carbon presenting a large volume of microporosity and narrow mesoporosity along with efficient packing density, exhibit maximum methane adsorption at high pressure, giving values of 167 cm^3 (STP)/cm^3 at 4 MPa. The empirical findings of this article complement those of earlier studies.

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